



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

**0 124 916
B1**

12

EUROPEAN PATENT SPECIFICATION

45 Date of publication of patent specification: 30.12.86

51 Int. Cl.⁴: C 08 L 71/04, C 09 K 21/12

21 Application number: 84200309.7

22 Date of filing: 05.03.84

54 Flame retardant polyphenylene ether composition.

30 Priority: 04.05.83 NL 8301569

44 Date of publication of application:
14.11.84 Bulletin 84/46

46 Publication of the grant of the patent:
30.12.86 Bulletin 86/52

84 Designated Contracting States:
BE DE FR GB IT NL SE

50 References cited:
WO-A-81/02020
FR-A-2 373 583
FR-A-2 426 069
GB-A-2 005 286
GB-A-2 060 656

70 Proprietor: GENERAL ELECTRIC COMPANY
1 River Road
Schenectady New York 12305 (US)

72 Inventor: Bussink, Jan
General Electric Plastics B.V. P.O. Box 117
NL-4600 AC Bergen op Zoom (NL)
Inventor: De Munck, Johannes Wilhelmus J.
General Electric Plastics B.V. P.O. Box 117
NL-4600 AC Bergen op Zoom (NL)

74 Representative: Grever, Frederik
General Electric Plastics B.V. P.O. Box 117
NL-4600 AC Bergen op Zoom (NL)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Leamington Spa, England.

EP 0 124 916 B1

Description

The invention relates to a polymer composition having flame-retarding properties, suitable for wire insulation extrusion, based on polyphenylene ether. The invention also relates to an electrically conductive wire having an insulation of synthetic resin which is provided by wire insulation extrusion and is built up from the polymer composition according to the invention.

Known polymer compositions for wire insulation extrusion of electrically conductive wires comprise a polymer as a synthetic resin: so far, polyvinyl chloride and polyethylene have been used in particular as a polymer.

Special requirements are imposed upon polymer mixtures for wire insulation extrusion: it must be possible to process the mixture by wire insulation extrusion, the mixture must have flame-retarding properties, after the wire insulation extrusion the mixture must have an elongation of more than 100%, the mixture should not be sensitive to strain corrosion and aging and must have a good impact strength. In some applications the requirement is imposed that the polymer mixture may not comprise any halogen atoms.

The invention provides a polymer composition based on a polyphenylene ether which satisfies the above-mentioned requirements.

The polymer composition according to the invention is characterized in that it comprises the following constituents: 50—70 parts by weight of polyphenylene ether, 0—20 parts by weight of polystyrene or a saturated-rubber-modified polystyrene, 25—45 parts by weight of a hydrogenated block copolymer having blocks consisting of homopolymers or copolymers of vinyl aromatic hydrocarbons and having blocks derived from a conjugated diene, 10—20 parts by weight of aromatic phosphate compound, 2—10 parts by weight of mineral oil, 0—10 parts by weight of typical additives.

The polymer compositions according to the invention cannot be formed into an article by injection moulding. When the polymer compositions according to the invention are injection-moulded, delamination occurs. On the other hand, the polymer compositions according to the invention can well be processed by wire insulation extrusion without noticeable delamination occurring.

To be preferred is a polymer composition which comprises 50—65 parts by weight of polyphenylene ether 5—15 parts by weight of homopolystyrene, 30—40 parts by weight of hydrogenated block copolymer, 15—20 parts by weight of aromatic phosphate compound, 4—8 parts by weight of mineral oil and 0—5 parts by weight of the typical additives.

Polymer compositions which comprises a polyphenylene ether, polystyrene, or a rubber-modified polystyrene, a hydrogenated block copolymer and an aromatic phosphate compound are known *per se*. For this purpose, reference may be made to United States Patent Specification 4,143,095 and the German Patent Applications 24 34 848 and 30 38 551. The polymer compositions described in these patent publications are extruded to pellets and are then formed into an article by injection moulding.

These known polymer compositions are not suitable for wire insulation extrusion because in one or more respects they do not satisfy the above-mentioned requirements for materials which are suitable for being provided around an electrical conductor by wire insulation extrusion.

Polymer compositions which comprise a polyphenylene ether, a block copolymer and a mineral oil, are known from the PCT Patent Application WO 81/02020. These known polymer compositions are also extruded to pellets and are formed into articles by means of injection moulding. However, these known polymer compositions are not suitable as a wire insulation for electrical conductors.

Polyphenylene ethers and their preparation are known *per se* from a large number of patent publications, *inter alia* from the United States Patent Specifications 3,306,874, 3,306,875, 3,257,357 and 3,257,358. The polymer composition according to the invention may comprise one or more of the known polyphenylene ethers, notably also homopolymers and copolymers. The polyphenylene ether in the polymer composition according to the invention preferably comprises units derived from 2,6-dimethyl phenol.

The polymer compositions according to the invention may comprise polystyrenes or a saturated-rubbermodified polystyrene. Polystyrene is to be understood to mean in this Specification homopolymers and copolymers comprising units derived from styrene or substituted styrene compounds, for example alpha-methyl styrene. All the known copolymers of styrene with the exception of the copolymers which comprise unsaturated bonds may be used, for example styrene-acrylonitrile copolymers. Polystyrenes modified with saturated rubbers are known *per se*. Examples are the polystyrene compounds saturated with EPDM rubber or ethylene-ethylacrylate rubber.

Hydrogenated block copolymers suitable for the polymer compositions according to the invention comprise blocks built up from a vinyl aromatic compound, for example, styrene, and blocks built up from a hydrogenated diene compound, for example butadiene. Suitable are linear block copolymers, radial teleblock copolymers and so-called "tapered" block copolymers, i.e. block copolymers built up from blocks which are bonded together via a "random" copolymer of the vinyl aromatic compound and (hydrogenated) diene compound. Suitable block copolymers are commercially available, for example from Shell under the name of Kraton G®.

Suitable aromatic phosphate compounds which are present in the polymer compositions according to

the invention are described, for example in United States Patent Specification 4,143,095. Triphenyl phosphate and diphenyl cresyl phosphate may be mentioned in particular.

The polymer compositions according to the invention comprise a comparatively large quantity of mineral oil. In combination with the above-mentioned constituents and the above-mentioned relative quantities of the said constituents, a polymer composition is obtained having the properties desired for wire insulation extrusion, due to the presence of the mineral oil. As a mineral oil there may be used aromatic, naphthenic and paraffinic oils or a mixture of one or more of such oils. Paraffinic and/or naphthenic oils are to be preferred.

In addition to the above-mentioned constituents, the polymer compositions according to the invention may also comprise further additives which are typical for compositions comprising polyphenylene ether. Stabilizing additives, for example phosphites, and metal compounds (ZnO, ZnS), dyes and pigments, lubricants may be mentioned in particular.

The invention will now be described in greater detail with reference to the following specific examples: Examples I to XI; comparative examples 1 and 2.

Various polymer compositions were prepared as indicated in Table A hereinafter: the polymer compositions I to XI according to the invention and the polymer compositions 1 and 2 for comparison.

The polymer compositions were prepared by dry-mixing the indicated constituents in a mixer until a homogeneous composition was obtained. These homogeneous compositions were then extruded by means of a double blade extruder type Werner-Pfleiderer ZSK 28 having a special kneading and dispersing blade. The blade of the extruder was rotated at a speed of 200—400 rpm; the temperature of the extruder was adjusted at 240—320°C; flow rate 5—25 kg per hour. The extrudate was cooled with water and chopped to form a granulate.

Test samples were manufactured from the resulting extrudate by injection moulding (T 250—300°C) and a few properties were determined.

The various extrudates as mentioned hereinbefore were provided around an electrically conductive copper wire by means of a wire insulation extrusion device as is generally used to insulate an electrically conductive wire with PVC. The copper wire was preheated at 60—110°C; the extrusion temperature was approximately 250°C. The resulting wire insulation was evaluated for its appearance. The wire insulation was removed from the copper wire and the elongation of the wire insulation was determined (elongation at rupture).

All results are recorded in Table B below.

From the data of Table B it is apparent that all polymer compositions according to the invention after wire insulation extrusion have a sufficient elongation; the comparative samples have too low an elongation value. It may be seen from a comparison of the results obtained in Examples VIII, IX and X that the use of paraffinic or naphthenic oils is to be preferred instead of aromatic oils. This appears from a more favourable value of the elongation of the insulation. All polymer compositions have good to very good flame retarding properties as appears from the indicated UL (Underwriters Laboratories) 94 and the LOI values (ASTM D2863).

TABLE A

Example	1	2	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
Composition in parts by weight													
Polyphenylene ether (poly 2,6-dimethylphenylene ether)	50	65	50	65	50	65	50	50	50	50	50	50	50
homopolystyrene	15	0	15	0	15	0	15	15	5	10	10	10	0
EPDM-rubber (9—10%)-modified polystyrene	0	0	0	0	0	0	0	0	0	0	0	0	15
hydrogenated styrene butadiene triblock copolymer	25	25	25	25	25	25	25	25	35	30	30	30	25
mixture of diphenylcresyl phosphate and triphenyl phosphate	10	10	10	10	10	10	15	20	15	15	15	15	15
paraffinic oil	0	0	4	4	8	8	4	4	4	4	0	0	4
naphthenic oil	0	0	0	0	0	0	0	0	0	0	4	0	0
aromatic oil	0	0	0	0	0	0	0	0	0	0	0	4	0
organic phosphite	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
ZnO	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
ZnS	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15

TABLE B

Example	1	2	1	II	III	IV	V	VI	VII	VIII	IX	X	XI
Properties of test pieces manufactured by injection moulding													
Izod impact strength with notch ASTM D256	615	600	595	570	540	550	605	590	605	610	595	595	615
Thermal deformation temperature 1,82 N/mm ² , ASTM D 648 °C	107	126.5	98.5	107.5	87	99.3	82	73.5	80.5	81.5	82	80.5	85
UL 94 1.6 mm sec.	23-3	17-14	27-15	27-15	41-1	28-13	21-10	13-7	54-7	34-4	36-8	27-4	29-8
LOI (ASTM D2863) %	34.5	36	32.8	35	32	33.5	33	34	32	31.5	31	32.8	31.5
Tensile strength at flow DIN 53455 mPa	46.5	45.5	38	41	31	33	34	33	28	32	34	36	33
Elongation at rupture DIN 53455 %	45	44	68	60	70	76	75	80	106	82	86	70	98
Melt viscosity 240°C, 4500 sec ⁻¹ Pa.s	360	500	300	360	240	300	215	170	255	235	240	225	230
Properties insulation after wire insulation extrusion													
Surface	not smooth	not smooth	good	reason- able	good	not smooth	good	very good	good	good	good	good	good
Elongation at rupture %	40	60	100	120	250	120	260	250	350	250	250	230	300

Claims

1. A polymer composition having flame-retarding properties, suitable for wire insulation extrusion, based on polyphenylene ether, characterized in that the polymer composition comprises the following constituents: 50—70 parts by weight of polyphenylene ether, 0—20 parts by weight of polystyrene or a saturated-rubber-modified polystyrene, 25—45 parts by weight of a hydrogenated block copolymer having blocks consisting of homopolymers or copolymers of vinyl aromatic hydrocarbons and having blocks derived from a conjugated diene, 10—20 parts by weight of aromatic phosphate compound, 2—10 parts by weight of mineral oil, 0—10 parts by weight of the typical additives.
2. A polymer composition as claimed in Claim 1, characterized in that the composition comprises 50—65 parts by weight of polyphenylene ether, 5—15 parts by weight of homopolystyrene, 30—40 parts by weight of hydrogenated block copolymer, 15—20 parts by weight of aromatic phosphate compound, 4—8 parts by weight of mineral oil and 0—5 parts by weight of the typical additives.
3. An electrically conductive wire comprising an insulation of synthetic resin provided by wire insulation extrusion, characterized in that the insulation of synthetic resin comprising a polymer composition comprising the following constituents: 50—70 parts by weight of polyphenylene ether, 0—20 parts by weight of polystyrene or a saturated-rubber-modified polystyrene, 25—45 parts by weight of a hydrogenated block copolymer having blocks consisting of homopolymers or copolymers of vinyl aromatic hydrocarbons and having blocks derived from a conjugated diene, 10—20 parts by weight of aromatic phosphate compound, 2—10 parts by weight of mineral oil, 0—10 parts by weight of the typical additives.

Patentansprüche

1. Polymerzusammensetzung mit flammhemmenden Eigenschaften, die für die Extrusion von Drahtisolierungen geeignet ist auf der Basis von Polyphenylenäther, dadurch gekennzeichnet, daß die Polymerzusammensetzung die folgenden Bestandteile aufweist: Gew.-Teile Polyphenylenäther, 0—20 Gew.-Teile Polystyrol oder ein gesättigtes gummi-modifiziertes Polystyrol, 25—45 Gew.-Teile eines hydrierten Blockcopolymeren mit Blöcken aus Homopolymeren oder Copolymeren von vinylaromatischen Kohlenwasserstoffen und mit Blöcken, die von einem konjugierten Dien abgeleitet sind, 10—20 Gewichtsteile aromatischer Phosphatverbindung, 2—20 Gew.-Teile Mineralöl, 0—10 Gew.-Teile typischer Additive.
2. Polymerzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß die Zusammensetzung 50—65 Gew.-Teile Polyphenylenäther, 5—15 Gew.-Teile Homopolystyrol, 30—40 Gew.-Teile hydriertes Blockcopolymer, 15—20 Gew.-Teile aromatischer Phosphatverbindung, 4—8 Gew.-Teile Mineralöl und 0—5 Gew.-Teile typischer Additive enthält.
3. Elektrisch leitender Draht, der eine Isolierung aus synthetischem Harz aufweist, die durch Drahtisolierungsextrusion aufgebracht ist, dadurch gekennzeichnet, daß die Isolierung des synthetischen Harzes einer Polymerzusammensetzung umfaßt, die die folgenden Bestandteile enthält: 50—70 Gew.-Teile Polyphenylenäther, 0—20 Gew.-Teile Polystyrol oder ein gesättigtes gummi-modifiziertes Polystyrol, 25—45 Gew.-Teile eines hydrierten Blockcopolymeren mit Blöcken, bestehend aus Homopolymeren oder Copolymeren von vinylaromatischen Kohlenwasserstoffen und Blöcken, die von einem konjugierten Dien abgeleitet sind, 10—20 Gewichtsteile aromatischer Phosphatverbindung, 2—10 Gewichtsteile Mineralöl und 0—10 Gew.-Teile typischer Additive.

Revendications

1. Composition de polymère présentant des propriétés de résistance au feu, convenant pour l'extrusion d'isolant sur fil, à base de poly(oxyphénylène), caractérisée en ce que la composition de polymères comprend les constituants suivants: de 50 à 70 parties en poids de poly(oxyphénylène), de 0 à 20 parties en poids de polystyrène ou d'un polystyrène modifié au caoutchouc saturé, de 25 à 45 parties en poids d'un copolymère séquencé hydrogéné contenant des séquences constituées par des homopolymères ou des copolymères d'hydrocarbures vinyli aromatiques et contenant des séquences dérivés d'un diène conjugué, de 10 à 20 parties en poids d'un composé phosphate aromatique, de 2 à 10 parties en poids d'huile minérale, de 0 à 10 parties en poids des additifs classiques.
2. Composition de polymères selon la revendication 1, caractérisée en ce que la composition comprend de 50 à 65 parties en poids de poly(oxyphénylène), de 5 à 15 parties en poids d'homopolystyrène, de 30 à 40 parties en poids de copolymère séquencé hydrogéné, de 15 à 20 parties en poids de composé phosphate aromatique, de 4 à 8 parties en poids d'huile minérale et de 0 à 5 parties en poids des additifs classiques.
3. Fil électriquement conducteur comprenant un isolant de résine synthétique appliqué par extrusion d'isolant sur fil, caractérisé en ce que l'isolant de résine synthétique est constitué par une composition de polymères comprenant les constituants suivantes: de 50 à 70 parties en poids de poly(oxyphénylène), de 0 à 20 parties en poids de polystyrène ou d'un polystyrène modifié au caoutchouc saturé, de 25 à 45 parties

0 124 916

en poids d'un copolymère séquencé hydrogéné contenant des séquences constituées par des homopolymères ou des copolymères d'hydrocarbures vinyle aromatique et contenant des séquences dérivées d'un diène conjugué, de 10 à 20 parties en poids de composé phosphate aromatique, de 2 à 10 parties en poids d'huile minérale, de 0 à 10 parties en poids des additifs classiques.

5

10

15

20

25

30

35

40

45

50

55

60

65